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Danish Atomic Energy Commission

Research Establishment Risö

Metallurgy Department Annual Progress Report

for the Period Ending March 31st, 1971

July, 1971

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Danish Atomic Energy Commission
Research Establishment Risö

METALLURGY DEPARTMENT
ANNUAL PROGRESS REPORT

for the Period Ending March 31st, 1971

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INTRODUCTION

This annual report covers the activities of the Metallurgy Department at Risö during the period April 1st, 1970 to March 31st, 1971.

It is convenient to present the research and development work in three main groups:

Nuclear Materials Research
General Materials Research
Materials Technology

each of which is dealt with in a separate chapter. Each chapter begins with a brief summary of the activities.

The year has borne the impress of steady development in most sectors without essential changes in the allocation of effort. The many aspects of outward relations have been emphasized.

In the field of Nuclear Materials Research, work on uranium-dioxide/zircaloy fuel elements for water-cooled power reactors was continued with testing in the Halden Reactor, Norway, and in the DR 3 at Risö. The maximum burn-up achieved so far in the Halden Reactor is 17,700 MWD/t UO_2 and in the DR 3 18,000 MWD/t UO_2. Most of this work is carried out in collaboration with the Elsinore Shipbuilding and Engineering Co., Ltd. The development of dispersion-hardened zirconium alloys - carried out together with the UKAEA - was intensified. The strength of the alloys is clearly superior to that of conventional zircaloy materials. Investigations of the corrosion resistance in new zirconium alloys reached the stage of in-pile testing, and a corrosion rig is being constructed. The study of low-alloyed steel for pressure-vessel application has developed into a comprehensive investigation of embrittlement/structure relations.

In General Materials Research most projects are gathered within the framework of relation of structure to deformation and strength. This group comprises both experimental and theoretical studies, e.g. projects concerning dispersion and grain-boundary strengthening, computer simulation of grain-boundary structure and texture development, strengthening by fibre-reinforcement, and dislocation configurations at high and low temperature deformation. Other projects deal with more basic phenomena in materials for direct nuclear application. This applies for instance to the projects on acoustic emission, ductility of hydrided zircaloy-2 and influence of intermetallic particles on the corrosion behaviour of different zirconium alloys.

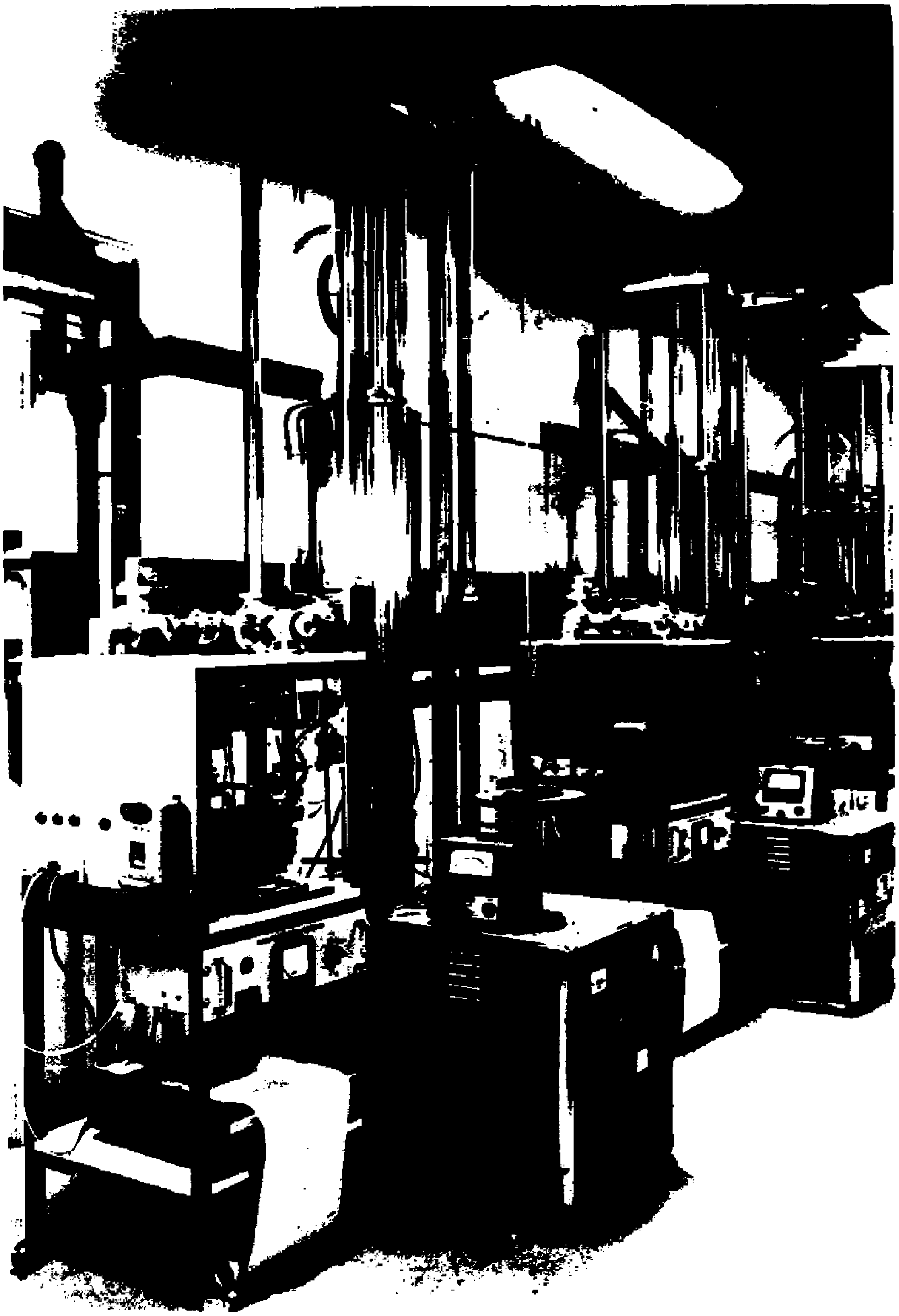

Fig. 1. New vacuum creep testing machines used in the zirconium work.

In the field of Materials Technology the previous results in non-destructive testing were followed up by the development of new equipment for contactless measurement of outer diameter and wall thickness of tubes.

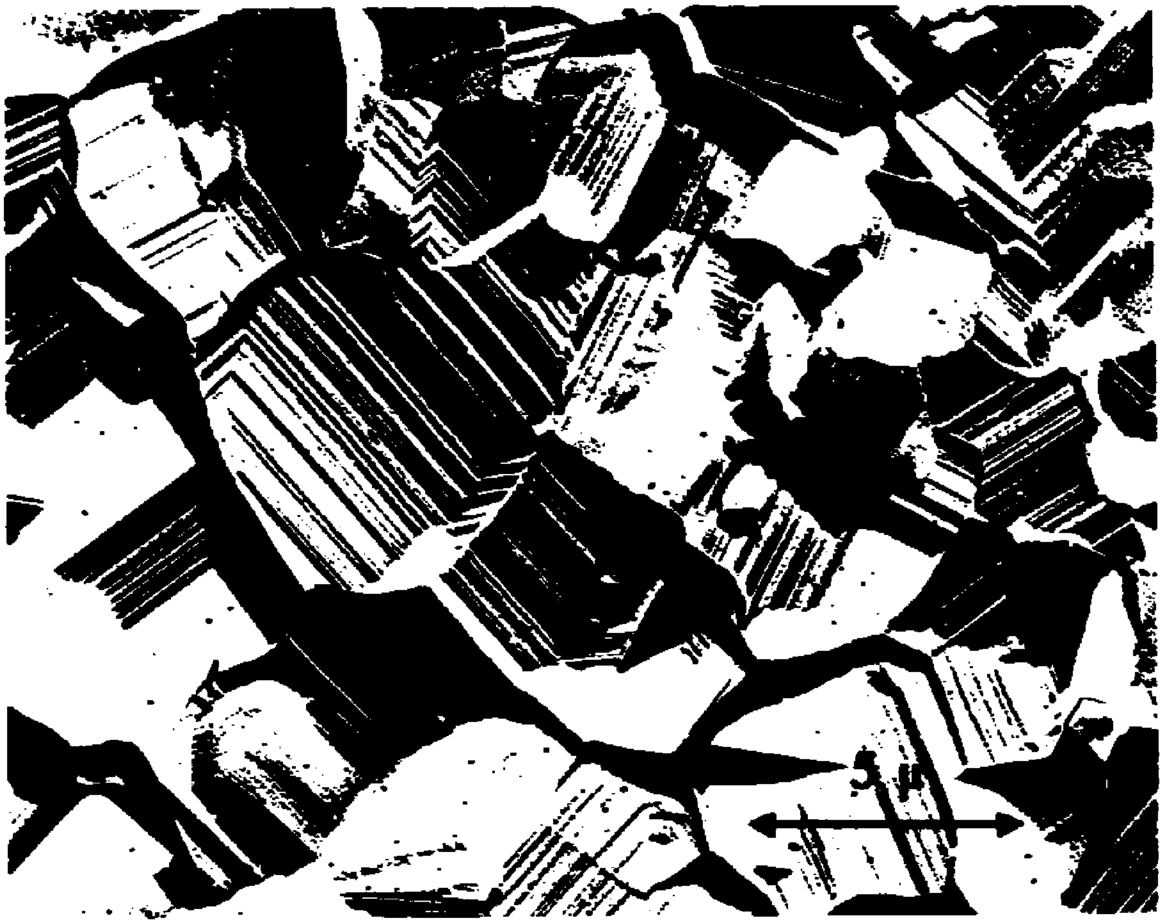

Fig. 2. Replica of magnesium oxide thermally etched during creep testing.

Also an automatic sand blasting equipment for removal of defective oxide layers on autoclaved zircaloy tubes was developed. The radiographic method of measuring uranium distribution in flat fuel elements was thoroughly investigated, and the technique for casting of uranium-aluminium alloys was improved so that a more uniform distribution was obtained.

Profitable expansion was made in the many important aspects of outward relations. Some of these, the participation in international collaboration and the engagement in education and training, are given a summarized description.

The participation of the department in international collaboration has hitherto been related almost entirely to nuclear application and safety aspects of reactors. This has now been extended to representation in a number of working groups and consulting committees on brazing, welding, brittle fracture of steel, fibre reinforcement, and general planning of development programmes in metallurgy.

The utilization of the expertise of the department for educational purposes has been emphasized. Members of the staff lecture at the Danish Academy of Engineering, and several pre- and post-graduate students have been working in the department.

The important contact with Danish industry was continued with collaboration and service programmes in many fields, e.g. materials development and testing, brazing, powder metallurgy and gas analysis.

In the internal administration of the department a number of working groups with various commissions (e.g. education, symposium arrangements, information, reception of visitors) have now been functioning for a period of about one year. Experience generally shows that the delegation of functions is fortunate.

NUCLEAR MATERIALS RESEARCH

The work within this field comprises development of uranium-dioxide/ zircaloy fuel elements for water-cooled reactors and materials development.

Fuel elements produced in co-operation with the Elsinore Shipbuilding and Engineering Co., Ltd., are being tested in the Halden Reactor in Norway. So far the maximum burn-up achieved is 17,700 MWD/t UO_2 (peak pellet). The in-pile testing also includes irradiation of fuel pins in the DR 3 Reactor at Risö. In addition, post-irradiation examination of a number of uranium-dioxide/zircaloy-2 fuel assemblies was carried out for foreign customers, including examination of assemblies with centre melting.

Zirconium alloys dispersion-hardened with yttrium oxide are being developed in collaboration with the UKAEA. After the commissioning of a new glove box, the production stages that are sensitive to atmospheric impurities can be carried out in an argon atmosphere with a total impurity content of the order of a few ppm. The evaluation of the properties of these alloys has now reached the stage where irradiation experiments are included. The zirconium development work also comprises corrosion testing of various new zirconium alloys, of which a Zr-Cr-Fe alloy was found to be most corrosion-resistant. A rig for in-pile corrosion testing of zirconium alloys is being constructed.

The irradiation embrittlement of a low-alloy Ni-Mo-V steel for potential pressure-vessel application is being studied. Specimens are heat-treated to different microstructures, and their ductile/brittle transition temperature is measured. Welding produces a special, technologically important heat treatment. Specimens were therefore cut from a weld to be included in the irradiation experiments.

Fuel Assembly Testing, Halden Irradiations

The status of the present Danish irradiation programme in HBWR is shown in table I. All assemblies have uranium-dioxide/zircaloy fuel pins. The maximum local burn-up, 17,700 MWD/t UO_2, was obtained with the assembly IFA 161.

Table I

Danish irradiation programme in HBWR

Fuel assembly designation	Loading date	Unloading date	Burn-up (MWD/t UO_2)	Heat load* range for major part of irradiation (W/cm)	Highest heat load* achieved (W/cm)
IFA 101	Nov. 67	Aug. 68	2,900	400-525	590
IFA 102	Nov. 67	May 69	6,800	400-525	610
IFA 147	Feb. 68	May 69	7,200	475-525	580
IFA 148	Feb. 68	-	12,800	400-525	575
IFA 161	June 68	-	14,400	500-575	615
IFA 162	June 68	Oct. 69	5,600	375-500	610
IFA 164	Jan. 69	-	7,500	325-425	480
IFA 165	Jan. 69	-	9,900	425-500	535
IFA 201	May 71	-	-	-	-
IFA 202	May 71	-	-	-	-

*Heat load at hottest pellet, calculated from recorded assembly power and form factors established by the Halden Project staff.

The eight assemblies loaded so far contain a total of 88 fuel pins. One of these failed, probably as a result of internal attack of fission product iodine. Pellet stacks in one assembly decreased by 0.6-0.9 % during irradiation; this is explained as a result of fuel/clad mechanical interaction leading to compressive creep of the uranium-dioxide. Details of fuel assembly design and post-irradiation examination are presented in Risö-M-1350.

Fuel Pin Testing, DR 3 Irradiations

Uranium-dioxide/zircaloy fuel pins with lengths up to 0.6 m and an outer diameter of 14 mm are being irradiated in the DR 3 Reactor in water-cooled rigs with nominal BWR conditions (70 atm., 285° C). The current programme comprises: (a) long-term irradiation (target burn-up 40,000 MWD/t UO_2) of standard pins at heat loads simulating the fuel shuffling conditions in commercial power reactors, (b) fuel/clad interaction studies, with investigation of various levels of pellet height to diameter ratio, clad temper and wall thickness, fuel/clad gap and heat load, (c) evaluation of the criteria for rejection at the fabrication stage because of welding and autoclaving defects, etc.

Table II

Summary of fuel pin irradiations in DR 3

Burn-up ($MWD/t\ UO_2$)	Number of pins	
	Unloaded	Still in reactor
Less than 1,000	15	2
1,000-5,000	18	6
5,000-10,000	0	2
10,000-15,000	0	0
More than 15,000	1	4
Total	34	14

The status of this progr^mme is summarized in table II. The maximum burn-ups achieved are 16,000 $MWD/t\ UO_2$ for a pellet pin and 18,000 $MWD/t\ UO_2$ for a vipac pin.

Post-Irradiation Examination of Uranium-Dioxide/Zircaloy-2 Fuel Assemblies (for foreign customers)

Post-irradiation examination of several test fuel assemblies was completed within the past year.

Among these assemblies two had been operating with melting in the uranium-dioxide core without failure for eleven months. One was a pellet fuel assembly, the other contained vibratory-compacted fuel.

In one of the pellet pins molten or plastic fuel was seen in contact with the cladding without any noticeable effect on the cladding material (fig. 3).

Fig. 3. Cladding in contact with strings of molten or plastic uranium dioxide. The cladding does not seem to be affected drastically at the contact points.

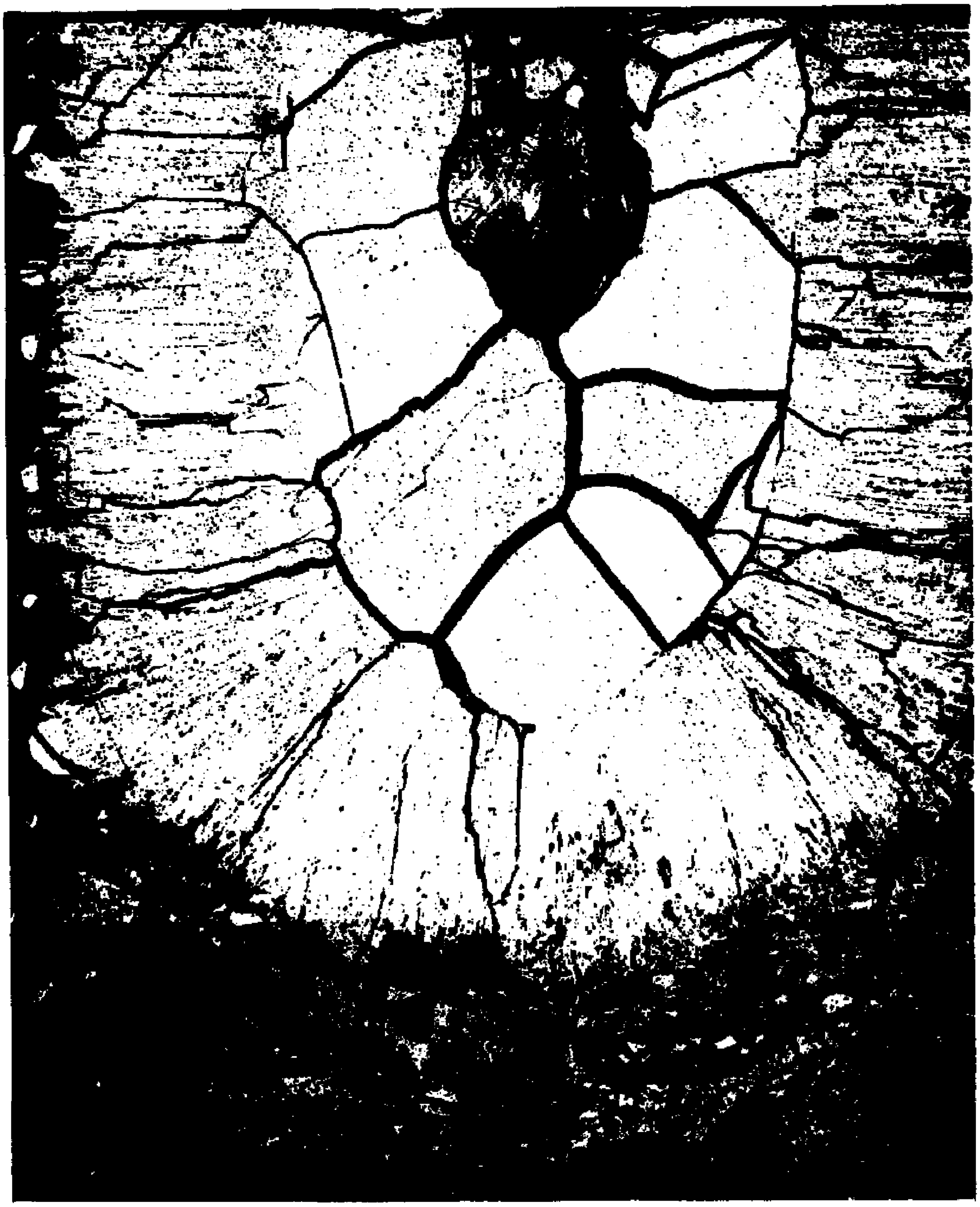

Fig. 4. 10% enriched vibratory-compacted fuel (white) in contact with natural uranium-dioxide pellet (grey). The temperature has been above the melting point in the centre of the enriched fuel. The central void that was formed during irradiation is partly filled with an inclusion of metallic fission products.

Contrary to this, corrosion attack and Widmanstätten structure were found in an area in one of the vipac pins where no molten fuel had been in contact with the cladding. Therefore the high temperature (about 900° C) in this area during operation was probably caused by film boiling of the coolant.

Fig. 4 shows the interaction zone between 10 % enriched vibratory-compacted fuel and natural pellet uranium-dioxide. The temperature in the enriched fuel had been sufficiently high to cause melting to a great extent (the dense zone) as well as formation of a central void, in which a large metallic inclusion of fission products can be seen.

Dragon Project Work

Post-irradiation examination of particle fuels as part of the Dragon Project consisted of metallography and deconsolidation of fuels from the experiment LEHPD-3 (low enrichment high power density) and from the third irradiation experiment 1C in the metallurgical series.

Examination of the eight types of loose particles in LEHPD-3 showed that an H.T.G.R. fuel will stand a burn-up of about 8 % fima (fissions per initial metal atom) in the case of the Dragon Reference design, but reduction of the coating thickness increased the tendency to failure. Fig. 5 shows a fuel particle after a burn-up of 8 % fima.

When the eight particle varieties were irradiated in the form of compacts, all fuel types survived the 8 % fima burn-up.

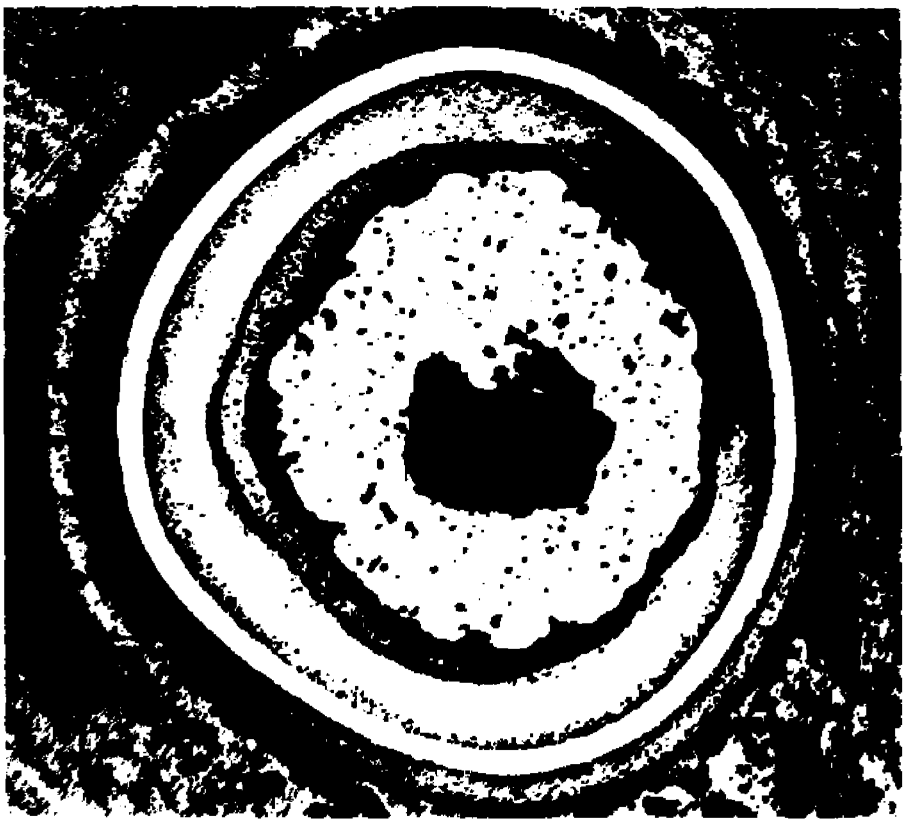

Fig. 5. Dragon fuel particle after a burn-up of 8% fima (x 100).

The element 1C was the third in the metallurgical series in which 42 different fuel and coating parameters were incorporated in the compacted fuel irradiated in the Dragon Reactor to a burn-up of between 7 and 11 % fima and a fast dose of about $3 \times 10^{21} \cdot n/cm^2$.

The object of the irradiation was to investigate long-term irradiation of coated particles in particular as far as parameters leading to spearhead attack are concerned. The experiment confirmed earlier results in this series: spearhead attack may be avoided by the introduction of a porous buffer layer of pyrocarbon adjacent to the fuel kernel or by increasing the deposition temperature of the inner coating.

In-Pile Corrosion Testing

In connection with the development work on zirconium alloys an in-pile rig for corrosion testing in steam and in water is under construction. It will be ready for operation in 1971.

It is well known that irradiation under certain conditions (depending on type of alloy, chemical environment and temperature) can enhance the corrosion rate of zirconium alloys, and therefore in-pile corrosion testing is a necessary step in the development of these alloys. As the enhancement factor usually depends on the oxidizing or reducing character of the environment, the rig is equipped with a water conditioning system (including ion exchanger, degasser and injection systems) by means of which the chemistry of the feed water can be adjusted as desired. The oxygen concentrations and the conductivity of the water is measured on-line, while other analyses will be carried out on samples taken from the system.

The rig will be positioned in a Mk. IV fuel element in the DR 3 Reactor. Maximum temperature and maximum pressure in the rig will be 450° C and 80 atm.

Corrosion Testing of New Zirconium Alloys

Several new zirconium alloys with corrosion resistance potentially superior to that of zircaloy-2 were investigated in high-temperature steam (500° C, 100 atm.) for up to 6000 hours as reported in the last annual report (Risö Report No. 225 (1970) 13-14).

The results indicate that the Zr-Cr-Fe materials (Zr-1.2 % Cr-0.12 % Fe) are the best high-temperature materials among the alloys tested. A quantitative comparison of the alloys with zircaloy-2 was not possible because of excessive spalling of the reference material at 500° C.

The Zr-Cu-Fe alloy showed transition at 840 hours and a weight gain of 210 mg/dm^2. The final weight gain after 6000 hours was 850 mg/dm^2. The Zr-V-Fe material showed transition after 2400 hours and a weight gain of 1200 mg/dm^2. Signs of spalling were observed at the end of this test. Zr-Cr-Fe materials from three different vendors (materials A, B and C) were investigated. Although the three materials were made according to the same material and process specification, they behaved differently. Materials A and B both exhibited two transition points on the weight-gain/time curve. For material A the transition points were found at 500 hours and 130 mg/dm^2 and at 3600 hours and 320 mg/dm^2, for material B at 700 hours and 110 mg/dm^2 and at 4500 hours and 360 mg/dm^2. The final weight gain after 6000 hours testing was 520 mg/dm^2 for A and 480 mg/dm^2 for B. Compared with these alloys, alloy C showed a remarkably different behaviour. It had only one transition point at 3200 hours and a weight gain of 170 mg/dm^2. The final weight gain was 320 mg/dm^2 and hence appreciably lower than those of A and B. We have at present no explanation of this difference.

Dispersion Strengthening of Zirconium Alloys

The programme was continued in collaboration with the UKAEA (RFL, Springfields). The major advances were the commissioning of a powder handling glove box fabricated in stainless steel, further measurements of strength properties of the alloys and investigations of their behaviour under neutron irradiation.

The vacuum-tight stainless-steel glove box (fig. 6) is connected to two furnaces, one for hydriding and one for vacuum sintering; a mass spectrometer unit is connected to the box for the continuous and rapid monitoring of impurities in the argon atmosphere used. The argon is circulated through a molecular sieve followed by heated titanium swarf in order to remove moisture, oxygen and nitrogen. A high-speed circulation pump ensures low humidity in the box during glove operation. The total impurity level in the box can be held below a few ppm.

The creep data obtained from powder-metallurgy-produced zircaloy-2/yttria alloys are shown in fig. 7. The data are compared with the results published by Shober et al. ("The Mechanical Properties of Zirconium and Zircaloy-2", BMI-1168 (1957)) on creep rupture at 500° C for zircaloy-2, 25 % cold-worked sheet and also zircaloy-2 bar annealed for 15 minutes at 750° C. The slope of the stress vs. time-to-rupture plot (fig. 7) for annealed zircaloy-2 is close to that of the powder-metallurgy alloys, but the slope of the cold-worked zircaloy-2 line indicates the inability of cold working to maintain the initially greater resistance to creep rupture over longer periods of time. At 500° C the powder-metallurgy-produced zircaloy-2/yttria alloys are clearly superior to the conventional zircaloy-2 alloys in the 25 % cold-worked or annealed conditions.

Irradiation experiments have just been completed in the DR 3. Tensile specimens of powder-metallurgy-produced zircaloy-2 containing 0, 5 and 10 v/o yttria and of commercial zircaloy-2 bar were irradiated at 285° C to an integrated neutron dose of 1.9×10^{20} n/cm^2 > 1 MeV, and the post-irradiation examination will cover tensile testing at elevated temperatures and metallography.

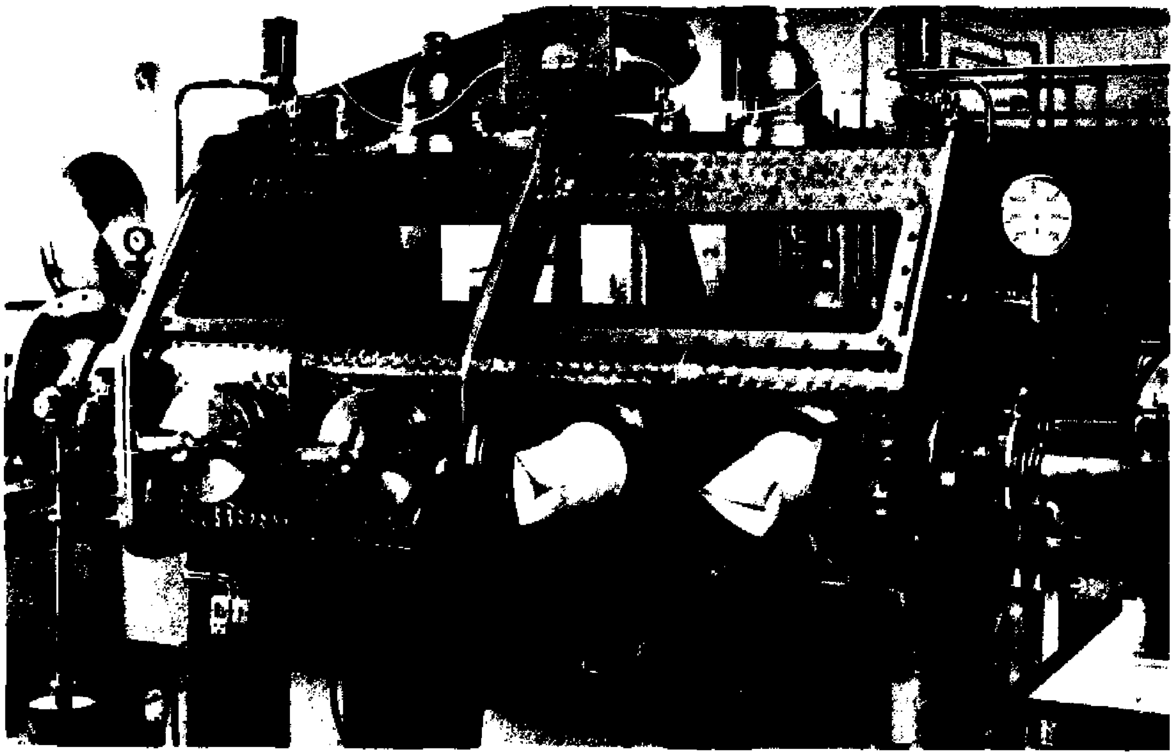

Fig. 6. Vacuum-tight glove box for powder handling in a pure argon atmosphere.

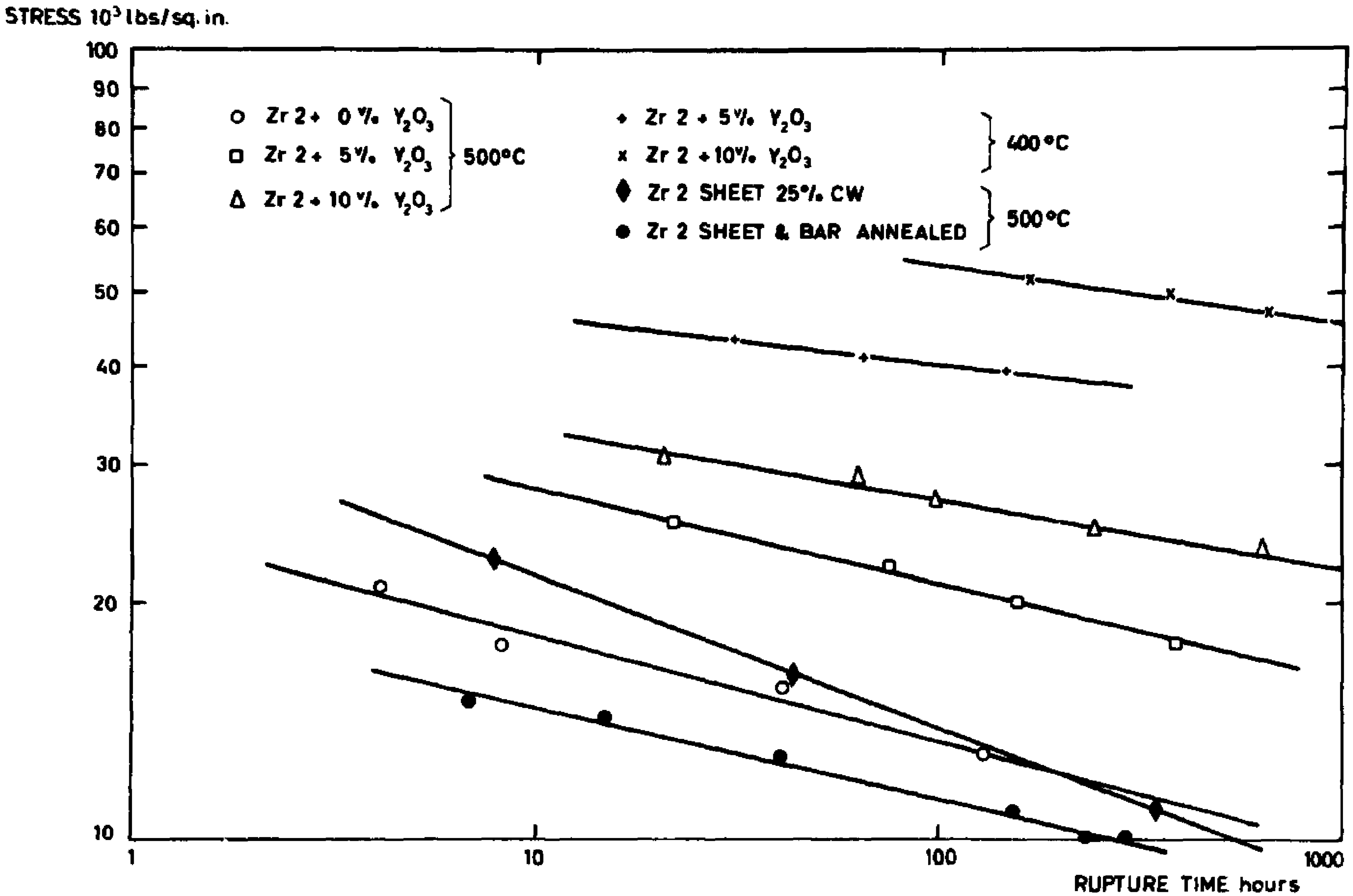

Fig. 7. Results of creep-to-rupture tests on dispersion-hardened zircaloy-2 and other zircaloy-2 materials.

Irradiation Embrittlement of a Low-Alloyed Steel Heat-Treated to Different Microstructures

For studies of the effect of different microstructures on irradiation embrittlement, specimens of the German low-alloyed steel BH70 were heat-treated to obtain, (1) tempered martensite, (2) tempered bainite and (3) tempered ferrite-pearlite. These specimens together with specimens in the as-delivered condition (quenched and tempered) were impact- and tensile-tested at different temperatures before and after irradiation.

The impact machine is equipped with a low-temperature apparatus for continuous variation of the specimen temperature from room temperature to -170° C. A temperature of -196° C is achieved by direct immersion in liquid nitrogen. Temperatures above room temperature are obtained by immersion in a silicon oil bath capable of reaching 300° C.

Results from the impact testing are shown in fig. 8.

The curves show a considerable increase in transition temperature (ΔTT at 4.2 kpm) for all four microstructures:

Tempered martensite	:	Δ TT = 135° C
Tempered ferrite-pearlite	:	Δ TT = 145° C
Tempered bainite	:	Δ TT = 135° C
Quenched and tempered	:	Δ TT = 140° C

Owing to the inherent scatter in this test method and to the similarity in ΔTT values, these results cannot be used for reliable ranking of the microstructures from the point of view of sensitivity to irradiation embrittlement.

Tensile tests are performed on an Instron testing machine from room temperature to -196° C. An attempt will be made to correlate the irradiation-induced changes in yield stress σ_Y and transition temperature according to a simple Ludwig-Davidenkov concept. - Corrections for the higher strain rate and greater triaxiality near the notch in the impact test will be made.

Irradiation of Weld Metal from the Low-Alloyed Steel BH 70

From a metallurgical viewpoint welded connections are considerably different from the base metal; moreover a welded connection is very inhomogeneous in structure, and this is true both for the remelted metal and for the heat-affected zones.

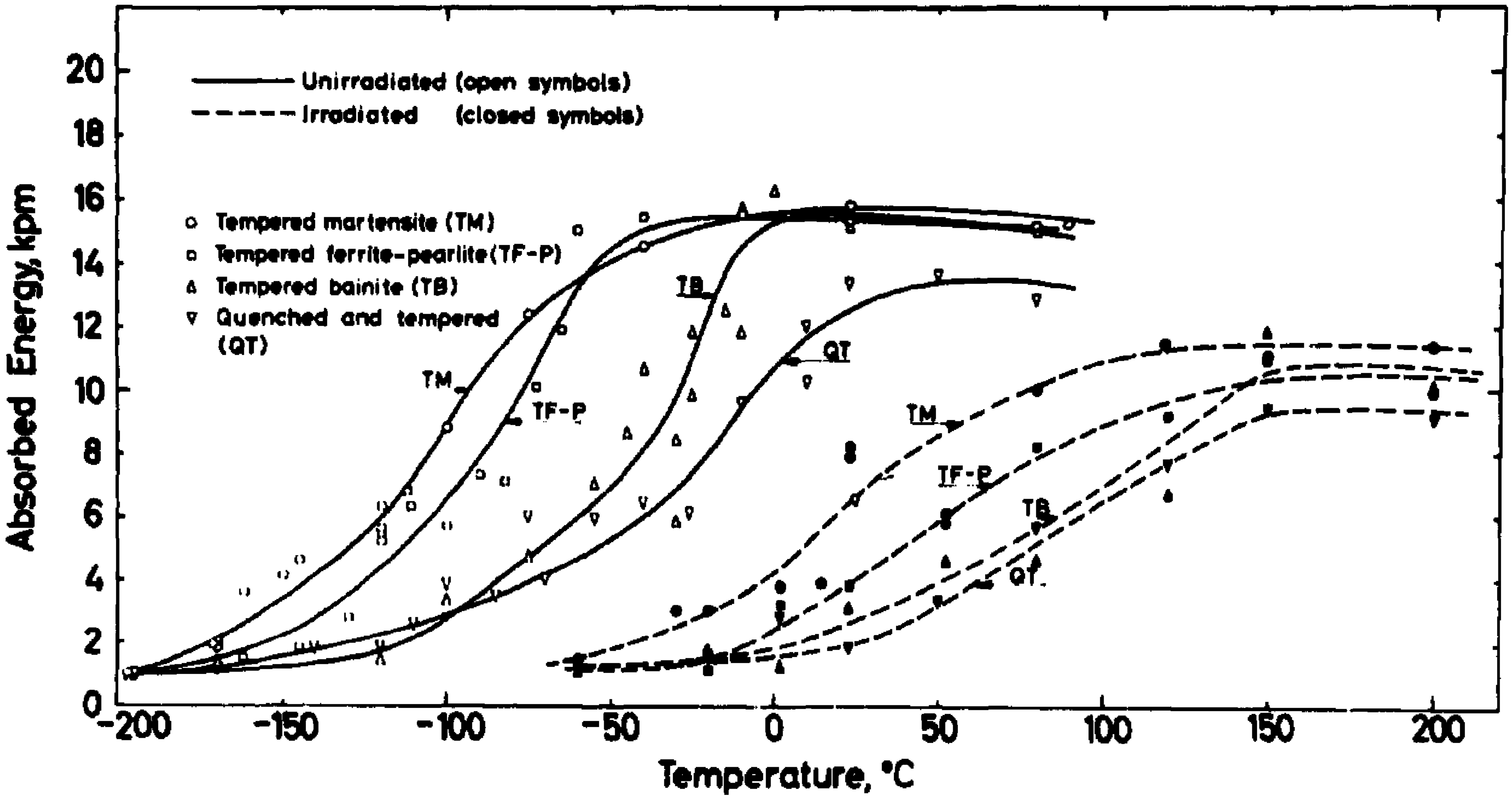

Fig. 8. Energy absorbed in impact test as a function of temperature for steel BH 70 heat-treated to different microstructures. Irradiation (to $4 \cdot 10^{19}$ $n \cdot cm^{-2}$ > 1 MeV at 390°C) causes a considerable increase in ductile/brittle transition temperature.

Fig. 9. Section of weld in 100-mm plate of BH 70 steel.

With the purpose of providing weld metal for irradiation experiments and gaining a wider knowledge of the weldability of the low-alloyed steel BH 70, welding of 100 mm plate of this steel was carried out in collaboration with the Danish Welding Institute.

Submerged arc welding was carried out as prescribed by the German works who produced the steel. The welding current was in this case not as high as usual, but limited to 600 A to keep the quality of the weld metal at a sufficiently high level. With the reduced welding current a rather large number of passes were necessary to fill up the large groove as seen on fig. 9 showing a section through the welded connection.

Test pieces for impact testing of the weld metal and the heat-affected zones are under preparation to be used for irradiation experiments.

GENERAL MATERIALS RESEARCH

This field covered investigations on mechanical properties of metals, alloys, ceramics and composites, basic studies of zirconium alloys of potential interest for fuel-element cladding, and some other studies. Furthermore, co-operation projects were initiated within specific areas of more practical nature.

Within the field of mechanical properties, a linear expression was established for the addition of different strength contributions. This result was obtained by reviewing the strength of alloys with dispersed particles, grain boundaries and solute elements, and checked on some experimental alloys. An extensive study of the creep properties of polycrystalline magnesium oxide was completed. The dislocation structure, consisting of a network of sessile and glissile segments, forms the basis of a creep model. The wide interest in grain boundaries initiated a study of the atomistic structure of grain boundaries by computer simulation.

A joint Scandinavian project was started on fibre-reinforced metals, aiming at a material for use at temperatures of about 1000° C. In the first stages of the project, the system nickel with tungsten fibres is used for basic studies of creep and fatigue.

Matrix Hardening in Dispersion-Strengthened Products

Dispersion hardening is one way of strengthening of soft matrix. Other strengthening processes such as grain-boundary hardening and solid-solution hardening are known. Experimental data for various dispersion-hardened systems were examined in order to investigate whether it is possible to add the stress contributions from these three different strengthening processes. The effect of dispersed particles was accounted for by the Orowan-expression $\sigma_p = \frac{G \cdot b}{\Lambda}$. The effect of grain boundaries was described by the Petch-expression $\sigma_{gb} = kD^{-\frac{1}{2}}$. The contribution from solid solution is entered as the value found empirically. Considering the flow stress values (0.2 % offset) it was determined to what extent the various contributions can be added independently, i. e. whether

$$\sigma = \sigma_o + \sigma_p + \sigma_{gb} + \text{sol}$$

is valid when inserting the stress values expected if the individual strengthening agents had occurred alone in the matrix. Data were obtained from the following systems: $Al\text{-}Al_2O_3$, $Ni\text{-}ThO_2$, $Zr\text{-}Y_2O_3$, and Fe-carbides. The upper limit for the amount of dispersed phase was about 10 v/o. The grain sizes were in the range from 0.3 µm to the order of 1 mm (obtained in extruded, cold-worked and recrystallized materials). Within certain limitations, the strength data at room temperature indicate that the contributions from the various strengthening agents can be added, i. e. that each mechanism acts independently. At higher temperatures in the range 0.5 to 0.8 T_m, the three strengthening processes may all contribute to the tensile strength and to the creep strength, but the use of the simple additive rule was inconclusive. At temperatures above 0.8 T_m, dispersion hardening is predominant.

Superposition of Grain-Boundary Strengthening and Particle Network Strengthening in Aluminium

Particle strengthening of a soft matrix can be obtained by having the particles uniformly dispersed or distributed in a three-dimensional network. In the first case it was found that grain-/subgrain-boundary strengthening and particle strengthening are approximately linearly additive. In the second case where grain boundaries and oxide boundaries are superimposed, the following equation was derived for the flow stress:

$$\sigma = \sigma_o + \sqrt{\sigma_p^2 + \sigma_{gb}^2} \tag{1}$$

where σ_p is the stress contribution from the particle network equal to $k_p \cdot t_p^{-\frac{1}{2}}$ where k_p is a constant and t_p is the mesh size of the particle network, and σ_{gb} is the stress contribution from the grain boundaries equal to $k_{gb} t_{gb}^{-\frac{1}{2}}$ where k_{gb} is a constant and t_{gb} is the grain size.

Data were obtained from six aluminium/aluminium-oxide products containing from 0.2 to 1.2 w/o aluminium oxide by measuring the flow stress (0.2 % offset) at room temperature and at 400° C. A reasonable agreement was found between the experimental values and the values calculated by inserting in equation (1) the individual contributions from the two strengthening mechanisms.

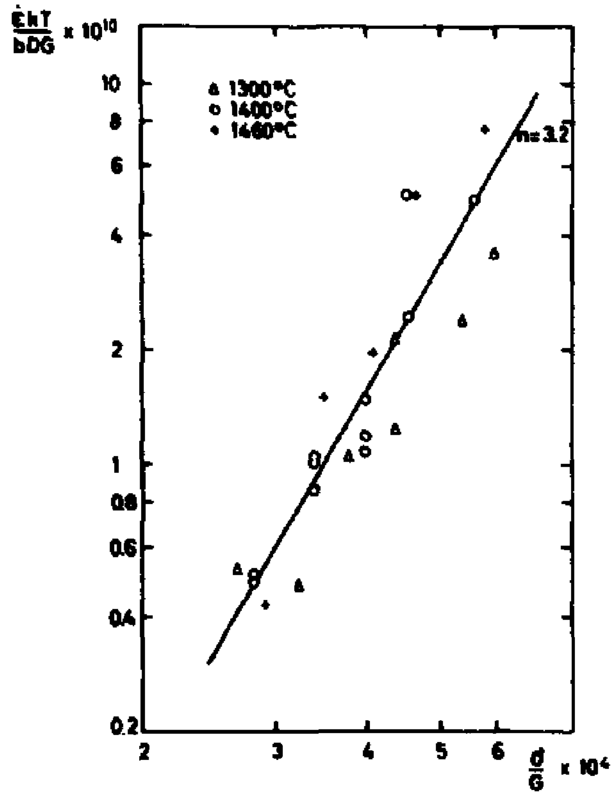

Fig. 10. log ($\dot{\epsilon}$kT/bDG) versus log (σ/G) for compressive creep testing of magnesium oxide. The slope (determined by a least-squares fit) is 3.2.

Creep of Polycrystalline Magnesium Oxide

The compressive creep testing of fully dense, polycrystalline MgO in the temperature range 1300-1460^{o} C under loads of 2.5 to 6 kp/mm^2 was continued. For the range of parameters investigated, the creep rate was independent of grain size (90 and 200 μm) and could be described with the following equation, in which D is the self-diffusion coefficient for oxygen ions:

$$\frac{\dot{\epsilon}kT}{bDG} = 12 \left(\frac{\sigma}{G}\right)^{3.2} \qquad \text{(see fig. 10).}$$

An investigation of the dislocation structure by transmission electron microscopy showed that a large number of the dislocations in the Frank network inside the subgrains are of mainly edge character, and that they lie in the plane perpendicular to their Burgers vector. These sessile dislocations are probably formed by the reaction

$$\frac{a}{2} < 110 > + \frac{a}{2} < \bar{1}01 > \rightarrow \frac{a}{2} < 011 > .$$

On the basis of this structure a mechanism was proposed in which glide accounts for the main part of the deformation although the creep rate is controlled by the annealing of the dislocation network and therefore diffusion-controlled. The creep rate calculated from this model differs from that of the Nabarro-Bardeen-Herring model only by a numerical factor of approximately 6.

The Structure of Grain Boundaries

The grain boundaries are of great importance for the properties of solids (strength, creep behaviour, diffusion, precipitation reactions). Knowledge of the atomistic structure of grain boundaries is therefore important for the understanding of these effects. At present there are, however, no experimental methods that can give direct information about the atomistic grain-boundary structure.

From grain-boundary-independent bulk properties the forces between the atoms in crystalline materials are known reasonably well. This suggests a possible approach to the grain-boundary structure, namely the synthesis of boundaries on a theoretical basis. In practice such a many-body problem can be solved in a digital computer.

In the present work the grain boundaries are produced by computer-simulated solidification of a liquid between two crystalline slabs of different orientation. Temperature and pressure are adjusted at relevant values during the computer experiment. In the running-in period the programme has been tested by solidification of a liquid between two identically oriented crystal slabs. The programme now works as intended.

The investigation is carried out in collaboration with the Department of Structural Properties of Materials at the Technical University of Denmark.

Ductility of Hydrided Zircaloy-2

The zirconium-hydride phase transformation is studied as part of an investigation of the ductile/brittle transition in hydrided zircaloy-2.

The preparation of samples of hydrided zircaloy-2 caused some trouble. Tentatively electrolytic hydriding was used, but the results turned out not to be sufficiently reproduceable. An apparatus for gas hydriding has now been constructed permitting the introduction of the desired hydrogen content to an accuracy of ± 5 %. The desired morphology and orientation of the hydride is obtained by a final anneal at 550° C. With the aim of studying the hydride phase transformation, techniques for high-temperature strain gauge dilatometry were developed, and the first results have been obtained. *It was shown that under zero stress conditions the hydride phase transformation* from the low-temperature γ' phase to the high-temperature δ phase occurs in the temperature region 280°C-360°C for zircaloy-2 hydrided to a level of 250 ppm of hydrogen ~ 1 w/o zirconium hydride. It was also found that the shape of the experimental curve of specimen extension against temperature closely parallels the predicted theoretical curve.

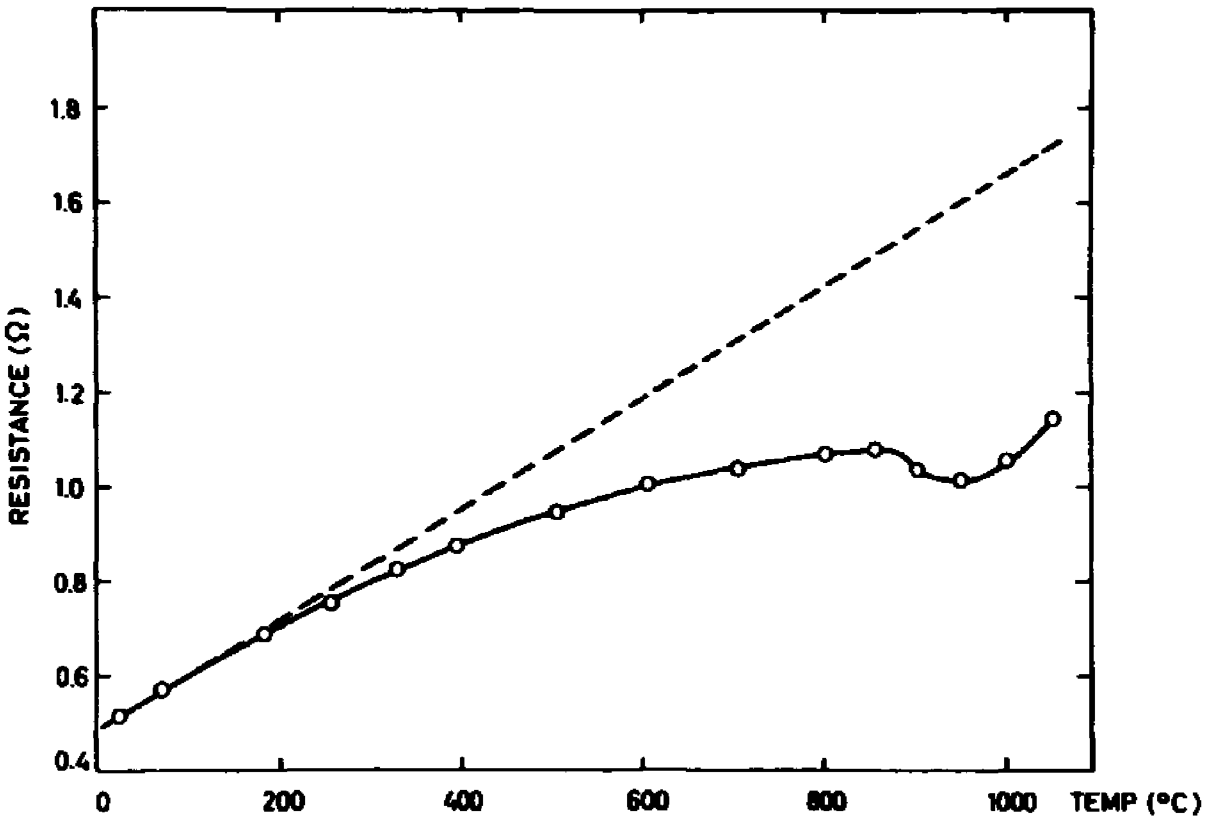

Fig. 11. Resistance versus temperature during heating of solution-treated and quenched zirconium-chromium-iron.

Precipitation Reactions in Zirconium-Chromium-Iron

The first stage in the investigation of the precipitation reactions is a solution treatment of the strip specimens followed by a rapid quench (up to 5000° C/sec). This stage is now under complete control.

The precipitation reactions (formation of $ZrCr_2$ and $ZrFe_2$) during slow heating will be followed by resistivity measurements. In the absence of reactions, resistance would increase linearly with temperature. Precipitation or clustering of solute atoms will tend to make the resistance decrease (or increase less with temperature) as already shown for other alloy systems. The techniques for resistance versus temperature measurements are being perfected. A preliminary result is shown in fig. 11. Between 200 and 800° C the resistance is reduced as compared with the linear curve on account of clustering and precipitation. The region 800-950° C is complicated by the α-β phase transition. Above 950° C the precipitates start redissolving, and the resistance increases steeply.

Influence of Particle Size and Corrosive Medium on the Corrosion Resistance of Zirconium-Chromium-Iron

Zr-Cr-Fe material was subjected to different heat treatments ranging from fast quenching to slow furnace cooling in order to change the intermetallic particle size in the matrix. Particle sizes in the range 0.5-50 μm were obtained. Specimens were subjected to oxidation treatment in pure oxygen and superheated steam in order to study the influence of particle size and corrosive medium on corrosion resistance.

The investigation revealed that when tested in pure oxygen, specimens containing large particles showed a corrosion resistance superior to that of specimens with fine particles. The opposite result was obtained by testing in steam.

These surprising observations revealed the importance of the nature of the corrosive medium and the influence of the surface area of the particles. The specimens are awaiting further detailed examination.

Dispersion Strengthening of Stainless Steel

A 20/20 austenitic stainless steel dispersion-hardened with aluminium oxide particles is produced through a powder metallurgy route (see Risö Report No. 225 (1970) 25).

Tensile specimens are obtained from the fully densified extruded rods of various compositions (oxide content between 0 and 10 v/o). Before tensile testing, these specimens are annealed at 800° C for two hours in vacuum. The tensile testing is carried out at room temperature, 400, 500, 600, 700, and 800° C. The elevated-temperature tests are carried out in vacuum.

The room- and elevated-temperature tensile strengths of stainless steel specimens containing 5.0 v/o aluminium-oxide particles are considerably higher than the corresponding ones of as-cast conventional stainless steels. The variation of the tensile strength with testing temperatures shows a very slight decrease up to 500° C, beyond which there is a marked drop.

Transmission electron microscopy on the extruded and annealed specimens confirms the absence of dispersoid agglomeration during the processing and manufacturing stages. The dispersoid particles are found to be distributed mainly at the subgrain boundaries, and their size remains the same as the original; some particles are found to be distributed within the subgrains. The subgrain size varies between 0.2 and 0.5 μm.

Powder Compaction

It is of scientific interest and technological relevance to understand the pressure-compaction behaviour of powder composites containing particles of deforming and non-deforming types.

In a preliminary investigation on powder composites such as Fe-Al_2O_3, Fe-ZrO_2 and Ni-Al_2O_3, it was shown that the presence of ceramic particles restricts the shape distortion of the matrix particles and thus the pressure densification, the degree of restriction being a function of the amount of ceramic particles (i.e. the amount of non-deforming contact surface area). It should also be mentioned that the size of the ceramic particles plays an important role in the overall pressure densification of the powder composites investigated.

Acoustic Emission

Under certain conditions during loading of steel structures, acoustic signals of very high frequencies will be generated within the steel. The signals can be detected and registered by means of suitable transducers fixed to the surface of the steel.

For practical application of acoustic emission, it seems advisable to try to establish a wider knowledge of the metallurgical phenomena giving rise to these signals. For this purpose equipment was developed for use on very small test pieces that can be loaded to fracture with a transducer fixed on them. The loading must be as noiseless as possible in order to avoid covering of the weak acoustic signals from spurious noise. For this reason the tensile apparatus has only few moving mechanical parts, and the loading is hydraulic. The design and operation of the equipment is shown in fig. 12.

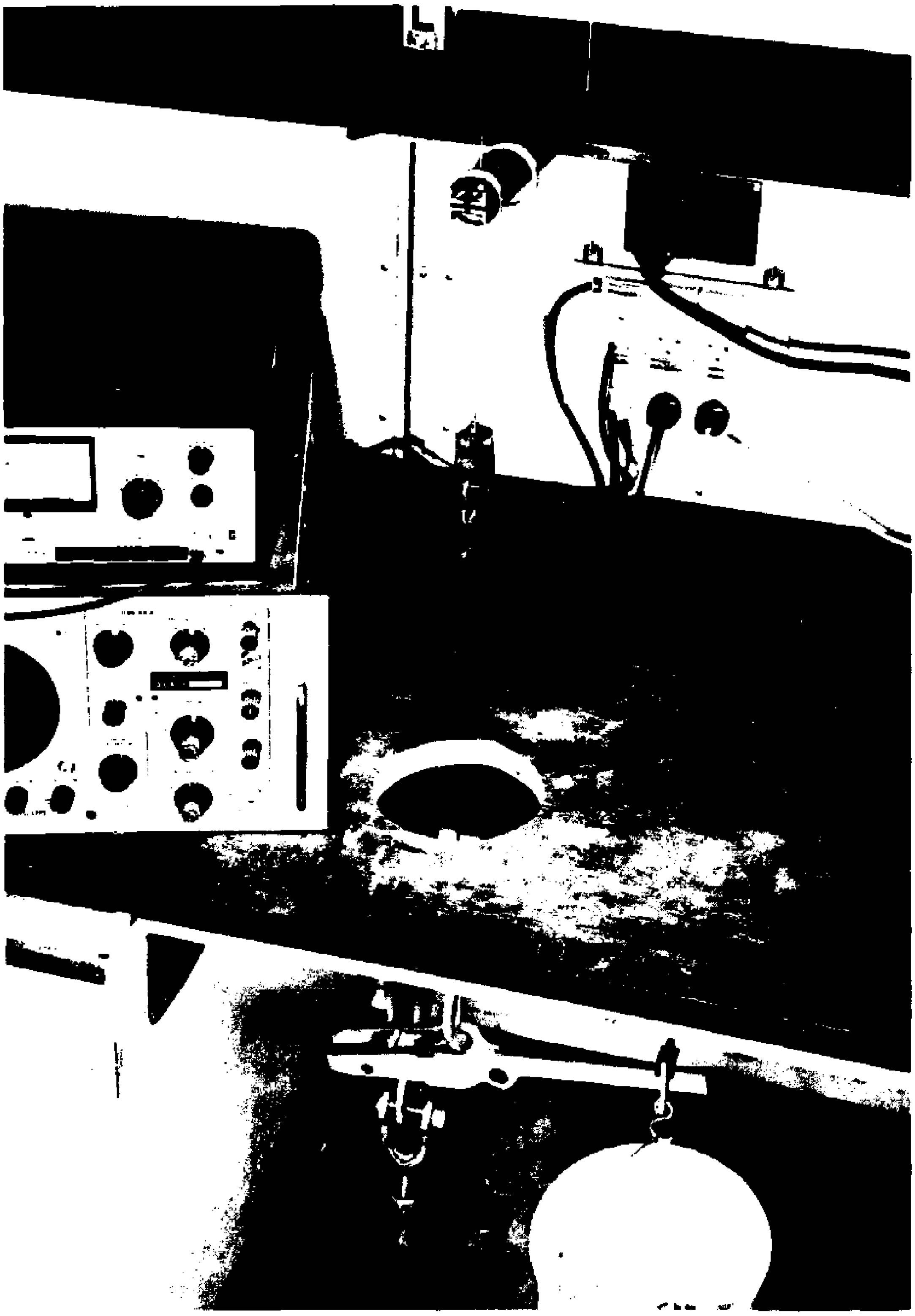

Fig. 12. Apparatus for tensile fracturing of mini specimens equipped with a transducer for registration of acoustic signals. Under the table is the hydraulic loading system - a water bucket.

MATERIALS TECHNOLOGY

The development work was concentrated on joining methods and non-destructive testing and control. Equipment including a high-frequency generator for vacuum brazing and brazing in reducing atmospheres was installed and used for contract work. Fundamental studies on shear strength, fatigue strength and impact strength of different brazed joints were continued.

In connection with the development of non-destructive testing and control methods, the beta back-scattering technique was successfully applied to particle size determinations in cement.

The manufacturing of fuel elements is now considered routine work, and during the year fuel pins of different designs and of lengths from 170 mm to 1800 mm were manufactured for irradiation in the DR 3 Reactor and the Halden Reactor. Furthermore, assistance was rendered to the Elsinore Shipbuilding and Engineering Co., Ltd., for manufacturing of the MTR-type fuel elements.

Casting of Uranium-Aluminium Alloys

This research programme, which was initiated last year, was brought to a level where acceptable results can be reproduced. The aim of the programme was to produce ingots in which the uranium content should be within ±0.4 % of the nominal value throughout the ingot. Ingots can now be produced with a uranium content which does not deviate by more than 0.3 % from the nominal value. The number of experiments was greatly reduced by use of the "Delphi-planning" principle.

The result is now used in the fuel plate manufacturing with favourable influence on cost and quality.

Wet Blast Cleaning of Autoclaved Zircaloy Tubes

Autoclaving is part of the production route of fuel pins. During this treatment a thin, black oxide layer is formed on the surface of the tube. In case of defects in the surface, the oxide layer turns brighter, and these tubes have so far been discarded. If the white oxide layer is caused by a defect that does not stretch deeper into the material, the tube might be used in the production if the defective oxide layer could be removed.

For this purpose, equipment for wet sandblasting was constructed. The sandblasting gives a clean metallic surface without removal of more than about 6 μm of the surface. The surface roughness remains small after sandblasting. The equipment works automatically and sandblasts tubes up to 4 metres long at a rate of 10 cm per minute. Aluminium oxide is used as blasting material. After renewed pickling and autoclaving, the tubes exhibit a good, shiny surface.

It is impossible to repair only part of the tubes as a new white area is formed at the boundary between the new and the old oxide layer (fig. 13).

From the fact that the white stains do not reappear after sandblasting it is concluded that they are not due to any inherent defect in the tube, and provided that the area is effectively wet blasted such tubes should be acceptable for reactor use. To prove this, a discoloured rejected tube was sandblasted and used for production of two mini pins. They are now being irradiated in the DR 3 Reactor to a planned total burn-up of 20-40,000 MWD/t UO_2.

Densitometric Method of Uranium Distribution Control in Flat Fuel Elements

Various factors that can influence the accuracy of uranium content measured by densitometric scanning of radiographs were investigated.

To ensure protection from scattered radiation, a special film casette with two aluminium strips as standards was constructed (see fig. 14). For longitudinal and transverse scanning of radiographs a special scanning bench with a commercial densitometer was constructed.

The intensity variation due to the varying focus/film distance (the radiographs are made on 72 cm long films from a distance of 82 cm) as well as the influence of processing conditions (developing time and temperature) on film contrast were investigated.

The uranium/aluminium equivalence curve produced will be used for the final assessment of uranium content in the fuel elements.

Fast and Accurate Equipment for Non-Destructive Inspection of Tubes

The main principles of the equipment are:

1) Avoidance of a probe inside the tube by calculation of internal diameter from exact measurement of outer diameter and wall thickness.

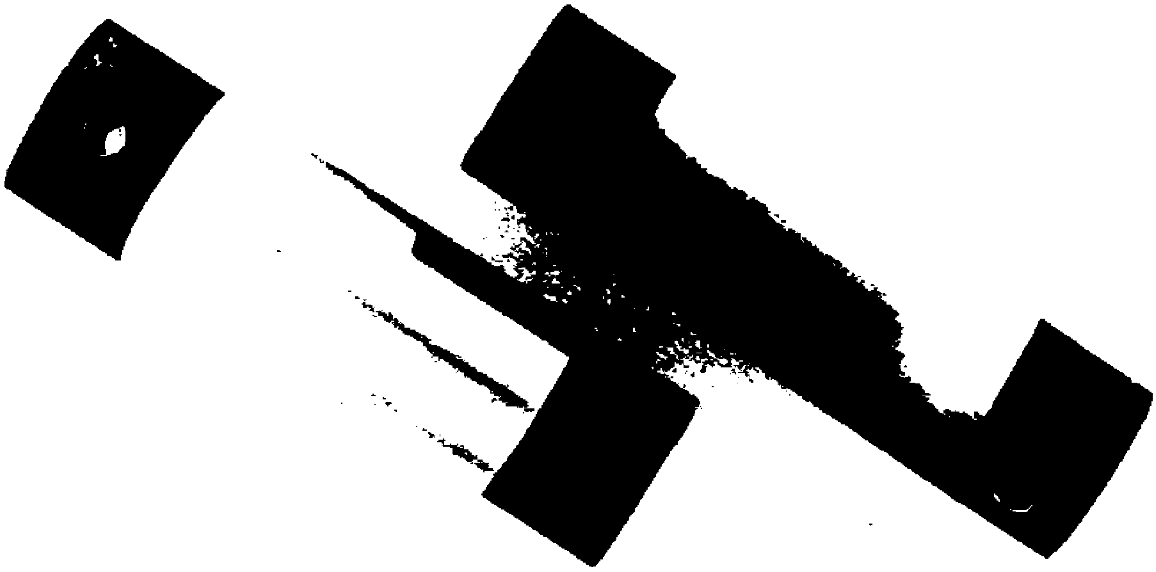

Fig. 13. Sandblasted and pickled zircaloy tubes. On the tube to the left the whole surface (except the protected areas at the ends) was sandblasted. On that to the right only part of the surface was sandblasted, resulting in an unacceptable transition zone around the sandblasted area.

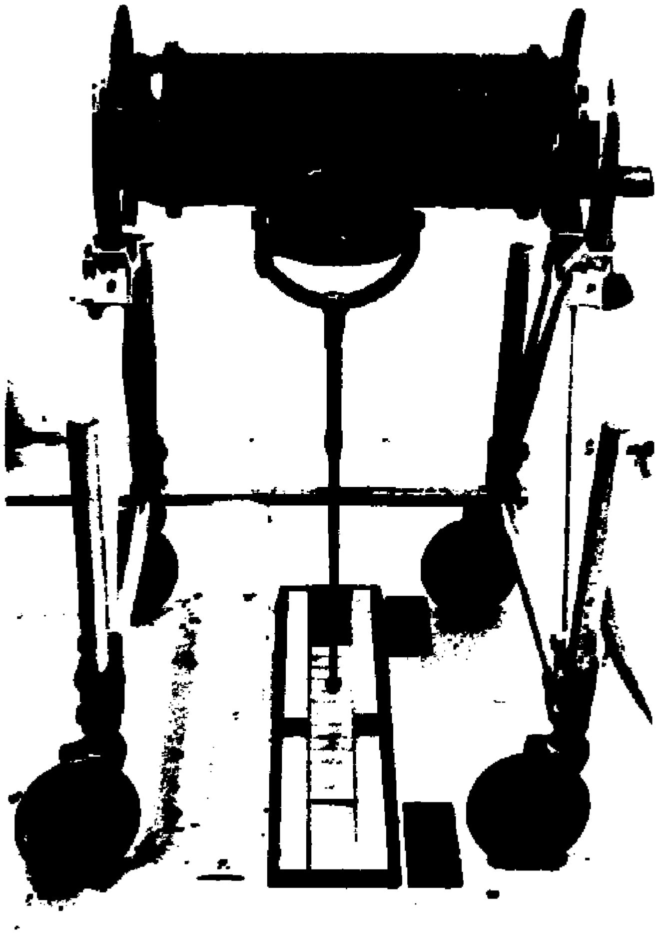

Fig. 14. Set-up for radiographic control of uranium distribution in fuel plates.

2) Rotation of probe instead of tube.

Three different methods were considered: The impulse-echo technique, the ultrasonic resonance method and the eddy current method.

The impulse-echo technique exhibits the best combination of speed, simplicity, linearity, and signal transmission. Therefore, the main effort is now being made in the improvement of the accuracy of this technique.

The ultrasonic resonance method was used for wall thickness measurements. The sweep frequency was raised from 50 to 1500 measurements per second, and the linearity of the signals was improved. Preliminary tests using this method for outer diameter measurements as well were carried out.

A computer programme was written for calculation of inner diameter from non-simultaneous measurements of wall thickness and outer diameter.

An eddy current probe with a linear signal was developed for accurate measurements of outer diameter. However, the method cannot be used for wall-thickness measurements.

Inner-Diameter Measurement

Within the more conventional field of inner-diameter measurement methods, the air-gauge technique was improved. With a mini-pressure transducer in the system placed next to the jets in the probe*), the dead volume of air was reduced to a minimum, and thus the inspection speed can be raised considerably (fig. 15).

As an alternative to the air-gauge measurement of the inner diameter, a method based on capacitive measurement with a commercial capacitance probe is examined with special regard to speed and accuracy.

The accuracy and reproducibility of measurements with the capacitance probe may be influenced by a number of factors.

Until now, stationary testing (capacitance probe in a fixed position in the tube) has been performed, and dynamic testing (tube moving with different rotation and translation speeds) has been started.

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*) Patent applied for.

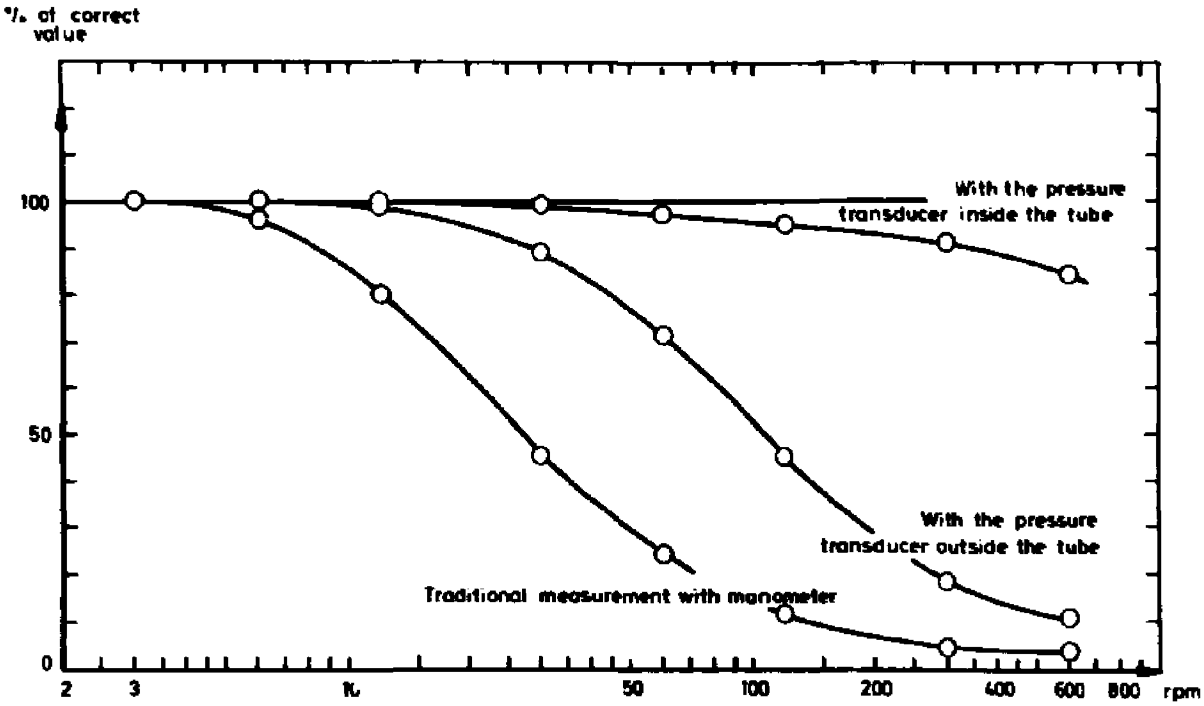

Fig. 15. As-measured inner diameter as a function of rotation speed for three different air-gauge techniques. When the transducer is inside the tube, the deviation from the true diameter is acceptably small up to high speeds of rotation.

PARTICIPATION IN INTERNATIONAL COLLABORATION

The department is engaged in the following types of international collaboration: joint technical projects, committee work, reception of research fellows, and technical and scientific meetings.

Participation in the ENEA reactor project at Halden was continued. Four Danish fuel elements are at the moment being tested under irradiation in the Halden Reactor. In the hot cells at Risö, elements irradiated at Halden by other signatories (Italy, Japan and the Federal Republic of Germany) were examined. The participation in the ENEA reactor project Dragon was continued, and a number of examinations of irradiated HTR fuel materials was carried out.

Joint technical projects were continued on post-irradiation examination of high-strength steel for pressure vessels and measurement of the thermal conductivity of uranium dioxide under irradiation (with AB Atomenergi, Sweden); also the programme, including irradiation tests, on dispersion-strengthened zirconium alloys (with the UKAEA) was continued with further characterization of mechanical properties. A joint programme was started for the examination of advanced zirconium alloys for water reactors (with the UKAEA, AB Atomenergi and the IFA, Norway). The department took part in a joint Scandinavian Nordforsk project on fibre reinforcement, and in a Scandinavian working group on hot cell techniques.

The department participated in the Halden Programme Group (member: N. Hansen), in the Halden Project's Working Group on Fuel (member: P. Knudsen), in the IAEA working group on "Engineering Aspects of Irradiation Embrittlement of Reactor Pressure Vessel Steels" (member: A. Nielsen), and in the following Technical Commissions of the IIW (International Institute of Welding): Commission I "Gas welding and allied processes", Sub-Commission A "Brazing and surfacing" (member: J. Christensen), Commission IX "Behaviour of metals subjected to welding", and Commission X "Residual stresses and stress relieving. Brittle fracture" (member: A. Nielsen).

Furthermore the department was represented in the CREST (Committee of Reactor Safety Techniques of ENEA) working group: "Material and mechanical problems related to the safety aspects of steel components in nuclear plants" (member: A. Nielsen). N. Hansen was a member of the working group under the EEC concerning technological collaboration, especially regarding metallurgy; the group put up proposals for research projects on materials for gas turbines, desalination plants and superconductors.

On grants made available by the Danish Atomic Energy Commission, three research fellows studied at the department. The research programmes covered steel for pressure vessels (M. Vacek, Czechoslovakia), fuel element studies (S. Mukhtar Ahmed, Pakistan), and creep behaviour of aluminium/aluminium-oxide alloys (B. Cech, Czechoslovakia).

EDUCATION AND TRAINING

Four members of the scientific staff of the department took part in teaching at institutes of higher education; this participation comprised regular lecturing on materials for students at the Danish Academy of Engineering and lecturing on materials at a post-graduate course arranged by Dansk Ingeniørforening (the Danish Society of Engineers). One member of the staff was the leader of a study group on "Brazing", arranged by Dansk Svejseteknisk Landsforening. Two staff members acted as external examiners at graduate examinations.

In the department a number of students worked on their examination projects:

Two students from the Department of Mechanical Technology of the Technical University of Denmark worked on "Salt Bath Brazing". Eight students from the Department of Mechanical Engineering of the Danish Academy of Engineering worked on the following projects: "Economical Evaluation of Iron Powder Production", "A Process Model for Fabrication of Nuclear Fuel Elements", "Investigation of the Strength of Glued Joints", "Automatic Particle Size Determination", "Recrystallization of Al/Al_2O_3 Alloys Containing a Three-Dimensional Network of Oxide Particles", "Construction of a Furnace for Casting Specimens of Fibre Reinforced Materials", "Mechanical Properties and Structure of Gold-Copper Alloys", "Characterizing of Iron Powders".

Two post-graduate students from the Technical University of Denmark worked in the department; one, from the Institute for Silicate Industry, completed his thesis on "Mechanical Properties of Ceramic Materials at Elevated Temperatures", and the other, from the Department of Structural Properties of Materials, started work on his thesis "Additive Strengthening Mechanisms in Dispersion-Strengthened Products".

Study groups were arranged in the fields of zirconium alloys, fuel element manufacture and behaviour and in physical metallurgy.

ORGANIZATION

(as at March 31)

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G. Holm Olsen
M. Simonsen

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M. Vacek [4]
B. Vigeholm

J. A. Aukdal
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J. Eskegaard
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J. Kjøller
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H. Lilholt
B. N. Singh
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J. Domanus [2]
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H. Jensen

Corrosion

K. Rørbo

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A. Rasmussen

Consultants

Gas analysis:	S. Kühnel Hagen
Welding:	E. Østgaard (Danish Central Welding Inst.)
Non-destructive testing:	N. Nielsen (Danish Central Welding Inst.)

1) On leave of absence from the UKAEA
2) On leave from the Elsinore Shipbuilding and Engineering Co., Ltd.
3) Post-graduate student from the Technical University of Denmark
4) IAEA research fellow from Czechoslovakia
5) On leave of absence at the AB Atomenergi, Studsvik
6) On leave of absence at the CEN, Saclay

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